# Charge-Transfer Absorption of Solid Ion Radical Salts. Application of One-Dimensional Hubbard Model

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The electronic spectrum of solid ion radical salt is known to be different from the monomer spectrum of the radical ion and to show an intermolecular charge-transfer band in the low-energy region. In order to understand the character of this charge-transfer absorption, one-dimensional Hubbard model was applied to such solid ion radical salt. The transition energy and the theoretical line shape of the charge-transfer absorption were derived and were compared with those of certain TCNQ anion radical salts.

The prominent magnetic, electrical, and optical properties of a number of solid ion radical salts have been the subject of many theoretical and experimental investigations over the past fifteen years.[1-5] In such ion radical salts, the planar ion radical molecules are known to form, in themselves, a plane-to-plane stacking into infinite one-dimensional columns so as to make a large overlap between their half-filled molecular orbitals.[6,7] In this case, since any individual radical molecule interacts through charge-transfer most strongly with two other neighboring radicals, the electronic spectrum of the solid salt differs distinctly from the monomer spectrum of the radical ion in solution but shows a charge-transfer transition between ion radicals in the low-energy region.[3-5]

In the present paper, we applied one-dimensional Hubbard model to the columns of ion radical molecules, and investigated the optical properties of solid ion radical salts. We attempted to explain the character of such charge-transfer absorptions on the basis of Green's function method. The transition energy and the theoretical absorption shape were compared with those observed for $\mathrm{K^+\ TCNQ^{\dot{-}}}$ anion radical salt, where TCNQ is 7,7,8,8-tetracyanoquinodimethane.

## Theoretical

In a narrow energy band with strong electron correlation, an electron transfers from one site to another site, but a strong repulsive force will take place when an electron happens to come onto a site which is already occupied by another electron with opposite spin. Let us denote the intra-site Coulomb repulsive energy as $I$, and consider a system of electrons described by the following Hamiltonian, which is often called the Hubbard Hamiltonian;[8,9)]

$$\mathscr{H} = \sum_{i,i,\sigma} t_{ij} C_{i\sigma}^{+} C_{j\sigma} + I \sum_{i} n_{i\downarrow} n_{i\uparrow}, \tag{1}$$

where $n_{i\sigma} = C_{i\sigma}{}^{+} C_{i\sigma}$, and $C_{i\sigma}{}^{+}$ and $C_{i\sigma}$ are the creation and annihilation operators of an electron with $\sigma$-spin at the $i$-th site, respectively, and where $t_{ij}$ is the transfer matrix element between the $i$-th and $j$-th sites, and the repulsive potential, $I$, appears only when two electrons are at the same site. We put $t_{ii}=0$ without loss of generality. The unperturbed band energy, $\varepsilon_k$, of the system is related to $t_{ij}$ by

$$\varepsilon_{k} = \sum_{j} t_{ij} \mathrm{e}^{i\boldsymbol{k}\cdot(\boldsymbol{R}_i - \boldsymbol{R}_j)}. \tag{2}$$

Hubbard studied, in his first paper (it is often referred to as Hubbard I),[8)] the one-particle Green's function of this system by using decoupling method of equation of motion. The Green function is given by

$$G_{k\sigma}(E) = \frac{1}{2\pi}\left\{\frac{E_{k\sigma}^{U} - I(1-n_{-\sigma})}{E_{k\sigma}^{U} - E_{k\sigma}^{L}} \frac{1}{E - E_{k\sigma}^{U}} + \frac{I(1-n_{-\sigma}) - E_{k\sigma}^{L}}{E_{k\sigma}^{U} - E_{k\sigma}^{L}} \frac{1}{E - E_{k\sigma}^{L}}\right\}, \tag{3}$$

where

$$n_{\sigma} = \langle n_{i\sigma} \rangle,$$

$$E_{k\sigma}^{U} = \frac{1}{2}\left(\varepsilon_k + I + \sqrt{\varepsilon_k^{2} + 2(2n_{-\sigma} - 1)\varepsilon_k I + I^2}\right),$$

$$E_{k\sigma}^{L} = \frac{1}{2}\left(\varepsilon_k + I - \sqrt{\varepsilon_k^{2} + 2(2n_{-\sigma} - 1)\varepsilon_k I + I^2}\right).$$

Here $E_{k\sigma}{}^{L}$ is the energy of an electron with $\sigma$-spin which moves about avoiding other electrons with $-\sigma$-spin, while $E_{k\sigma}{}^{U}$ is the energy of an electron which propagates mainly among sites already occupied with electrons with $-\sigma$-spin.

On the other hand, starting from Kubo's formula,[10)] Kubo expressed the conductivity tensor of the Hubbard Hamiltonian in terms of two-time Green's function.[11)] The spectrum of optical absorption from $E_{k\sigma}{}^{L}$ to $E_{k\sigma}{}^{U}$ (*i.e.*, the intermolecular charge-transfer absorption) is given by the real part of the diagonal element of the frequency-dependent conductivity tensor, $\mathrm{Re}\sigma_{xx}(\omega)$, that is,

$$\mathrm{Re}\sigma_{xx}(\omega) = \frac{e^2}{\pi V}\frac{1}{\omega}\sum_{k,\sigma} \delta(\omega - E_{k\sigma}^{U} + E_{k\sigma}^{L}) \times \frac{\delta E_{k\sigma}^{U}}{\delta k_x} \frac{\delta E_{k\sigma}^{L}}{\delta k_x}\{f(E_{k\sigma}^{U}) - f(E_{k\sigma}^{L})\}, \tag{4}$$

where $V$ is the volume of the system, and $f(E)$ is the Fermi distribution function.

In order to apply this theory to one-dimensional stacks of ion radical molecules, we consider non-alternant linear chain of sites for which the transfer matrix elements are assumed to exist only between nearest neighbor sites. In this case, the unperturbed band energy is given by

$$\varepsilon_k = 2T\cos ka, \qquad \left(-\frac{\pi}{a} \leq k \leq \frac{\pi}{a}\right), \tag{5}$$

where $T(<0)$ is the transfer matrix element between nearest neighbors and $a$ is the lattice separation. $\mathrm{Re}\ \sigma_{xx}(\omega)$ in Eq. 4 is composed of two contributions from the transitions of electrons with up and down spins. In the following, we only consider the contribution of electrons with up spin, but the optical absorption by electrons with up spin depends strongly upon $n_\downarrow$ through correlation effect. From the $\delta$-function of Eq. 4, an electron with a wave vector $\boldsymbol{k}$ absorbs the electromagnetic wave with the frequency $\omega$;

$$\omega^2 = \varepsilon_k{}^2 + 2(2n_\downarrow - 1)I\varepsilon_k + I^2. \tag{6}$$

This leads to

$$\varepsilon_k = \varepsilon^{\pm}(\omega) = -I(2n_\downarrow - 1) \pm \sqrt{\omega^2 - 4I^2 n_\downarrow(1-n_\downarrow)}. \tag{7}$$

The optical transition from $E_{k\sigma}{}^L$ to $E_{k\sigma}{}^U$ with the wave vector $\boldsymbol{k}$, which satisfies $\varepsilon_k = \varepsilon^+(\omega)$, gives the absorption

$$\mathrm{Re}\,\sigma^+(\omega) = \frac{e^2}{2}\frac{I^2 n_\downarrow(1-n_\downarrow)}{\omega^2\sqrt{\omega^2 - 4I^2 n_\downarrow(1-n_\downarrow)}}$$
$$\times\sqrt{4T^2 - \{-(2n_\downarrow - 1)I + \sqrt{\omega^2 - 4I^2 n_\downarrow(1-n_\downarrow)}\}^2}\,\theta_+(\omega), \tag{8}$$

where

$$\theta_\pm(\omega) = f(E_\pm{}^L) - f(E_\pm{}^U),$$

$$E_\pm{}^L = \frac{1}{2}\{\varepsilon^\pm(\omega) + I - \sqrt{(\varepsilon^\pm(\omega)+I)^2 - 4I(1-n_\downarrow)\varepsilon^\pm(\omega)}\},$$

$$E_\pm{}^U = \frac{1}{2}\{\varepsilon^\pm(\omega) + I + \sqrt{(\varepsilon^\pm(\omega)+I)^2 - 4I(1-n_\downarrow)\varepsilon^\pm(\omega)}\}.$$

In a similar way, the transition between the two states with the wave vector $\boldsymbol{k}$, which satisfies $\varepsilon_k = \varepsilon^-(\omega)$, gives the absorption

$$\mathrm{Re}\,\sigma^-(\omega) = \frac{e^2}{2}\frac{I^2 n_\downarrow(1-n_\downarrow)}{\omega^2\sqrt{\omega^2 - 4I^2 n_\downarrow(1-n_\downarrow)}}$$
$$\times\sqrt{4T^2 - \{-(2n_\downarrow - 1)I - \sqrt{\omega^2 - 4I^2 n_\downarrow(1-n_\downarrow)}\}^2}\,\theta_-(\omega). \tag{9}$$

Therefore, the total contribution to the optical absorption, $\mathrm{Re}\,\sigma_{xx}(\omega)$, due to the electrons with up spin is given by $\mathrm{Re}\,\sigma^+(\omega) + \mathrm{Re}\,\sigma^-(\omega)$.

## Discussion

In this section, we shall apply this theory to the optical properties of certain crystalline TCNQ anion radical salts. Let us consider, for example, a system of simple anion radical salt of $\mathrm{K^+TCNQ^{\dot{-}}}$. According to Anderson and Fritchie's X-ray analysis data,[6] the crystal structure of $\mathrm{K^+TCNQ^{\dot{-}}}$ belongs to the monoclinic system with space group $P2_1/n$. The structure consists of one-dimensional columns of $\mathrm{TCNQ^{\dot{-}}}$ ions parallel to the $a$ (needle) axis with a plane-to-plane stacking; the molecular normal vectors nearly coincide with the column axes. Each column is surrounded by four columns in which the $\mathrm{TCNQ^{\dot{-}}}$ ions are rotated by 90° from those in the central column. The potassium ions occupy sites between $\mathrm{TCNQ^{\dot{-}}}$ columns in such a manner that each $\mathrm{K^+}$ ion is surrounded by eight nitrogen atoms at the corners of a distorted cube.

On the other hand, each TCNQ anion radical molecule is almost planar, and has sixteen molecular orbitals for seventeen $2p\pi$ electrons.[12] Therefore, in the ground state, the molecular orbitals from the lowest to the 8th are fully occupied, while an unpaired electron is in the 9th molecular orbital. The other molecular orbitals are vacant orbitals.

In order to apply Hubbard model of Eq. 1 to the crystalline $\mathrm{K^+\ TCNQ^{\dot{-}}}$ anion radical salt, we consider the column of TCNQ anion radicals. We take only the 9th molecular orbital of the unpaired electron for one site of TCNQ anion radical, and assume a model of non-alternant one-dimensional column composed of infinite number of such sites. From the crystallographic data,[6] the intermolecular distance between nearest neighbor sites, $a$ in Eq. 5, is of the order of 3.4 Å. Therefore, in this model, each TCNQ anion radical site has one identical molecular orbital with equal energy level, and there is one electron per each site. Then, we have $n_\downarrow = 0.5$ if we assume a paramagnetic state for our system. Under these situations, we consider the optical absorption (charge-transfer absorption) of the crystalline $\mathrm{K^+TCNQ^{\dot{-}}}$ anion radical salt as expressed by Eqs. 8 and 9. By using $n_\downarrow = 0.5$, we can easily obtain

$$\mathrm{Re}\,\sigma^+(\omega) = \frac{e^2}{8}\frac{I^2}{\omega^2\sqrt{\omega^2 - I^2}}\sqrt{4T^2 - \omega^2 + I^2}\,\theta_+(\omega), \tag{10}$$

$$\mathrm{Re}\,\sigma^-(\omega) = \frac{e^2}{8}\frac{I^2}{\omega^2\sqrt{\omega^2 - I^2}}\sqrt{4T^2 - \omega^2 + I^2}\,\theta_-(\omega). \tag{11}$$

Here we assume, for the sake of simplicity, that the Coulomb repulsion potential is much greater than the band width, or we consider the absorption spectrum at very low temperature. In this case, $\theta_\pm(\omega) = 1$ so that both $\mathrm{Re}\,\sigma^+(\omega)$ and $\mathrm{Re}\,\sigma^-(\omega)$ in Eqs. 10 and 11 have the same absorption spectrum. Fig. 1 shows a schematic description of $\mathrm{Re}\,\sigma^+(\omega)$ or $\mathrm{Re}\,\sigma^-(\omega)$ *versus* $\omega$ for this case, as is shown by the (a) line. Therefore, the total contribution to the absorption spectrum, $\mathrm{Re}\,\sigma^+(\omega) + \mathrm{Re}\,\sigma^-(\omega)$, is given by the (b) line of Fig. 1.

As is shown in Fig. 1, the theoretical optical absorption due to the charge-transfer transition between TCNQ anion radical sites has a sharp divergent peak at the energy $\omega = I$, where the spectrum has a van Hove singularity in the lower energy side.[11] The spectrum has no absorption in the energy region $\omega < I$, but has an absorption intensity in the region $\omega > I$. The absorption intensity is the greatest at $\omega = I$, and decreases progressively with the increase of $\omega$. The highest energy of the absorption takes place at $\omega = \sqrt{I^2 + 4T^2}$,

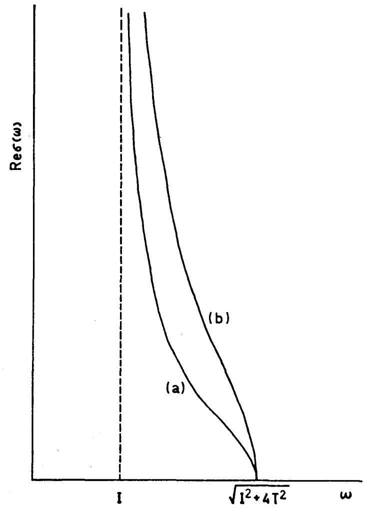

Fig. 1. The theoretical absorption line shape due to the charge-transfer transition between ion radical molecules in one-dimensional Hubbard model. Curve (a) indicates the spectrum of $\mathrm{Re}\,\sigma^+(w)$ of Eq. 10 or $\mathrm{Re}\,\sigma^-(w)$ of Eq. 11 with $\theta_\pm(w) = 1$, while curve (b), that of $\mathrm{Re}\,\sigma^+(w) + \mathrm{Re}\,\sigma^-(w)$. See text.

where the intensity falls down to zero. The spectrum has a shoulder in the region $I<\omega<\sqrt{I^2+4T^2}$. Therefore, the charge-transfer absorption has a width of $\sqrt{I^2+4T^2}-I$. This width is caused by the existence of non-zero transfer matrix element of $T$ in the unperturbed energy band of Eq. 5. In fact, if we assume $T=0$, that is, if we assume an independent site model in the unperturbed energy band, the absorption spectrum, $\mathrm{Re}\sigma^+(\omega)+\mathrm{Re}\sigma^-(\omega)$, is only a $\delta$-function at $\omega=I$ with no width, as this model requires.

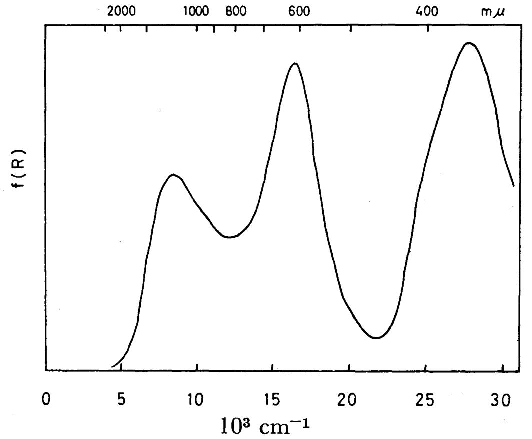

Fig. 2. The experimental result on the diffuse reflection spectrum of solid K$^+$ TCNQ$^{\overline{\cdot}}$ anion radical salt, where the value of Kubelka-Munk function, $f(R)=(1-R)^2/2R$, was plotted *versus* wave number ($10^3$ cm$^{-1}$ unit). See Ref. 3.

Let us compare these theoretical predictions with the experimental electronic spectrum of crystalline K$^+$ TCNQ$^{\overline{\cdot}}$ anion radical salt. In a previous paper,[3] we measured the electronic spectrum of this salt by means of diffuse reflection method. The observed spectrum is reproduced in Fig. 2. The Kubelka-Munk function, $f(R)=(1-R)^2/2R$, where $R$ is the reflectance and $f(R)$ is proportional to the absorbance, was plotted against the wave number ($10^3$ cm$^{-1}$ unit). In the energy region from 5000 to 30000 cm$^{-1}$ the solid-state spectrum of K$^+$ TCNQ$^{\overline{\cdot}}$ anion radical salt has three absorptions. The absorptions at 16400 and 27800 cm$^{-1}$ are the shifted bands of the monomer spectrum of the TCNQ anion radical at 11900 and 25300 cm$^{-1}$, respectively, while the low-energy band at 8500 cm$^{-1}$ characteristic of the solid salt has been assigned to the charge-transfer transition between TCNQ anion radicals in one-dimensional column.[3] If the theoretical absorption of Fig. 1 is applied to this characteristic low-energy band, the observed absorption peak value, 8500 cm$^{-1}$, should correspond to $\omega=I$, so that the intra-site Coulomb repulsive energy for the system of TCNQ anion radicals is estimated to be $I=8500$ cm$^{-1}$. As for the line shape and the line width, the theoretical spectrum has no absorption in the region $\omega<I$, while the observed charge-transfer absorption has a considerable width even in the energy region lower than its peak position. Moreover, the theoretical spectrum has absorption only in the region $I\leq\omega\leq\sqrt{I^2+4T^2}$ so that the line shape should be asymmetrical with respect to $\omega=I$. However, this asymmetric character is not obvious in the observed charge-transfer absorption, although the charge-transfer band overlaps with the higher-energy band of 16400 cm$^{-1}$. There may be several reasons for these discrepancies:

(1) An important one is that in our theory we assumed, as is shown in Eq. 4, a $\delta$-function for the elementary transition from $E_{k\sigma}{}^L$ to $E_{k\sigma}{}^U$ at each wave vector, while the actual elementary transition is not a $\delta$-function but involves finite width. In fact, the individual site in our Hubbard model is the TCNQ anion radical molecule composed of 20 atoms. Then, the elementary absorption may involve a width of vibrational structures due to the vibronic effect of the molecule.

(2) Another reason for the broadening of elementary transition at each wave vector comes from two electronic effects in the scattering process of an electron by those with opposite spin.[9] One is the effect of the randomness in the spacial distribution of electrons with opposite spin; Hubbard called it as the scattering correction. Another is the effect of the motion of electrons with opposite spin; he called it as the resonance broadening correction. These two electronic effects will also influence significantly the shape of charge-transfer absorption spectrum. We can make these corrections if we use the method proposed by Hubbard in his third paper.[9] There has been a relevant work made by Sadakata and Hanamura,[13] who examined the optical properties of three-dimensional half-filled band system for certain transition metal compounds.

(3) In the theoretical absorption spectrum of Fig. 1, we neglected the temperature effect and only considered the extreme case of $\theta_\pm(\omega)=1$. However, the experimental spectrum of Fig. 2 was observed at room temperature. Therefore, if we consider the effect of Fermi distribution term, $\theta_\pm(\omega)$, at finite temperature, the theoretical spectrum of Fig. 1 will become more smoothed.

At any rate, in the charge-transfer absorption of K$^+$ TCNQ$^{\overline{\cdot}}$ system, the observed line shape is almost symmetrical with respect to $\omega=I$. In this respect, the absorption line width due to the transfer matrix element, $\sqrt{I^2+4T^2}-I$, seems to be very narrow compared to the width due to the elementary transition, 3500 cm$^{-1}$, so that the $|T|$ value may be much less than 4200 cm$^{-1}$. As this $|T|$ value appears much less than the $I$ value, we can well see that a narrow band system with strong electron correlation takes place in such one-dimensional column of TCNQ anion radicals. On the other hand, however, it is very important to find certain crystalline ion radical salts where transfer matrix element is comparable to or larger than the width of elementary transition, because they will show asymmetric charge-transfer absorption with a shoulder in the high-energy region. Then we can estimate the magnitude of $T$ directly by analyzing such asymmetric line shape with our theoretical model, as long as the approximation for the Green function of Eq. 3 is applicable to our system.

So far, in order to apply simple one-dimensional Hubbard Hamiltonian of Eq. 1 to the crystalline K$^+$ TCNQ$^{\overline{\cdot}}$ salt, we have only considered the 9 th molecular orbital of the unpaired electron as one site of TCNQ anion radical, and neglected the other occupied and vacant molecular orbitals. This simple model solely leads to the optical properties of the charge-transfer transition between TCNQ anion radicals, but cannot explain the character of other higher-energy electronic transitions which arise mostly from local excitations of TCNQ anion radical molecules. Therefore, further theoretical treatment including all of the molecular orbitals is required to explain those higher-energy transitions as well as the low-energy charge-transfer transition in such crystalline ion radical salts.

In the present paper, we have only discussed the one-dimensional system of simple TCNQ anion radical salts, where each TCNQ anion radical has one unpaired electron so that each TCNQ site is equivalent. However, there are a number of complex TCNQ anion radical salts,[1,2] which include not only TCNQ anion radicals but also formally neutral TCNQ molecules so that each TCNQ site is no longer equivalent. In order to take into account this inequivalence, Soos and Klein modified the Hubbard Hamiltonian of Eq. 1 and studied the electronic states of less than half-filled band system for those complex TCNQ anion radical salts.[14] Therefore, we will also attempt to investigate, by extending our present method, the optical properties of such complex TCNQ anion radical salts.

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